STUDY OF THE PRODUCTION OF RESORCIN

BY

D. E. CABLE

J. I. PREST

ARMOUR INSTITUTE OF TECHNOLOGY

1918

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Study of the production of
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A Study of the Production of Resorcin

A THESIS

PRESENTED BY

DONALD E. CABLE AND J. IRVING PREST

TO THE

PRESIDENT AND FACULTY

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FOR THE DEGREE OF

BACHELOR OF SCIENCE

IN

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Table of Contents

	Page
Introduction	1
Part I	
An Attempt to Produce Resorcin from m Phenediamine by Means of the Bisulphite Conversion	
Introduction	6
Proposed Procedure	7
Experimental Work	9
Part II	
Present Commercial Method of Producing Resorcin	
Introduction	16
Theoretical Considerations	16
Experimental Work	19

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Introduction

The past few years, after the beginning of this present "world war", has seen a multitude of industrial problems thrust upon the chemists and chemical engineers of this country, due to the withdrawal of Germany from her extensive trade in chemicals and related products. The German chemical industries were so highly developed and organized that previous to this time our country, for various economical reasons, was not in a position to start, in any important degree, a competition with regard to the production of such goods to even supply our own market. This led to our absolute dependence upon Germany for the supply of many of these products which was most keenly felt when our trade relations were severed with that country. The problem of developing the manufacture of such materials in this country to satisfy the demand which had been created was presented

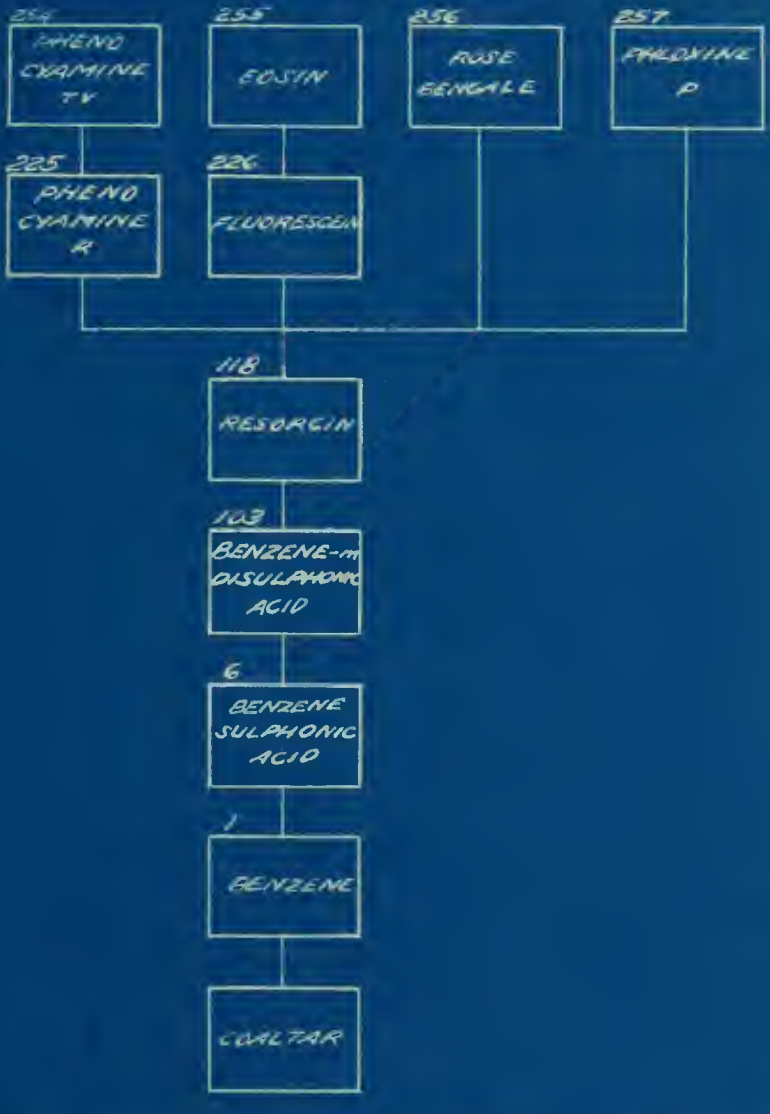
to the chemists of America to solve.

Those familiar with the progress made by the American Chemical industries have seen how successfully many of these problems have been handled. There are yet many which will demand years to master. It is one of these industrial problems to which the authors have devoted their attention in this thesis, and that is the manufacture of resorcin.

This material is a definite chemical compound and is the meta-dihydroxi derivative of benzene, its formula being, $C_6H_4(OH)_2$. Resorcin is of considerable commercial importance as a pharmaceutical product and an intermediate compound used in the manufacture of various "coal tar" dyes. It is derived commercially, by synthetic processes, from benzene and is made into various dyes by chemical combination with other chemical compounds. The relation of resorcin to some of the other products obtained from coal tar is well illustrated in Fig. I, which was taken from the chart prepared

FIG. 1

DERIVATION OF LEADING COAL TAR COLORS
ADAPTED FROM THE "COAL-TAR TREE" OF
H. VON BRUNCK



THE RESORCIN BRANCH OF THE IMPORTANT
COAL TAR DYES

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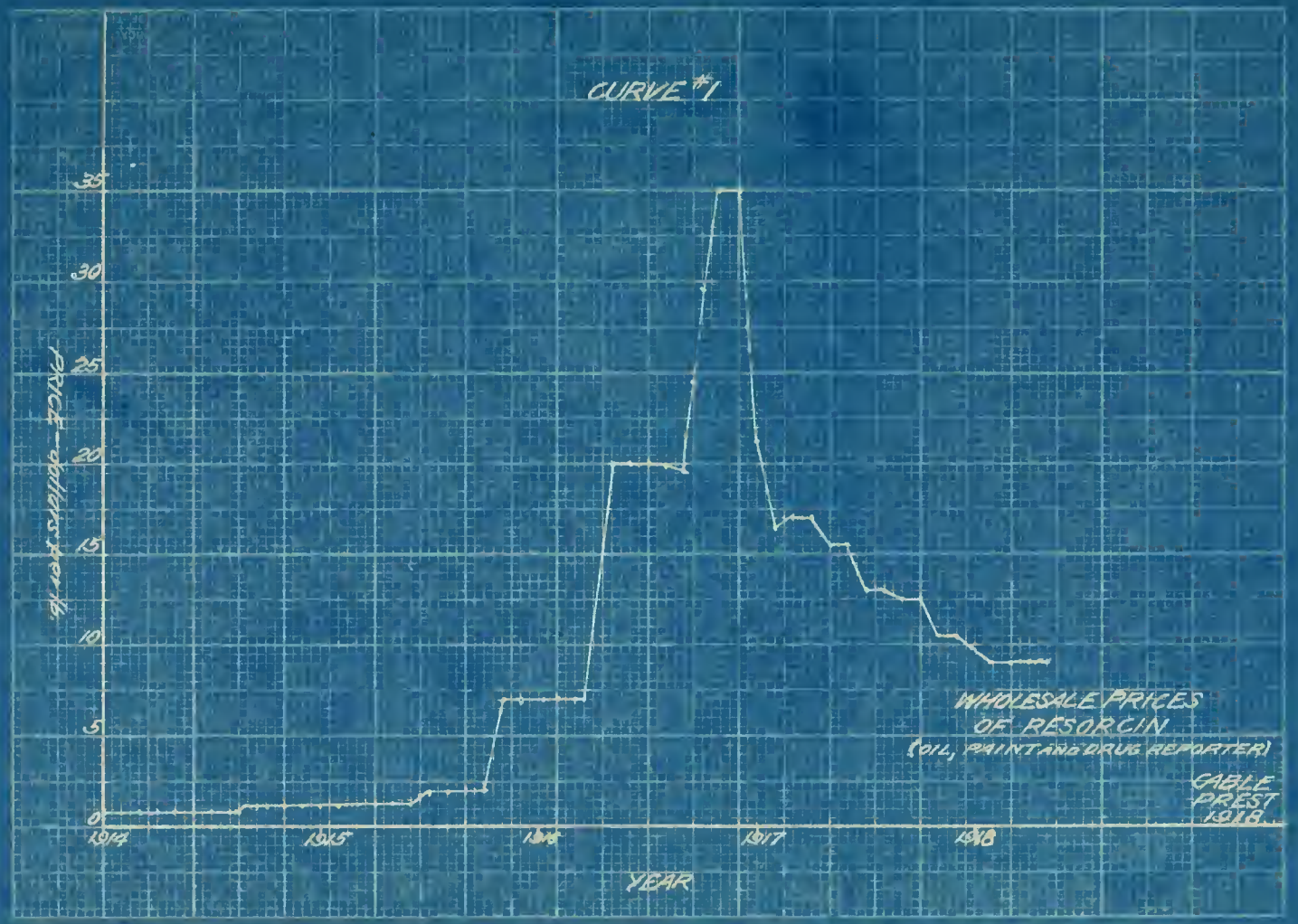
1918

by Thomas H. Norton, entitled "Derivativation of Leading Coal-Tar Colors, Adapted from the 'Coal-Tar Tree' of H von Brunck, Director of the Badische Aniline and Soda Fabrik", and found in the supplement to the issue of the Oil, Paint and Drug Reporter, October 2, 1916.

One of the reasons for regarding the manufacture of resorcin as being still unsatisfactorily solved lies in the fact that its market price has remained abnormally high as compared to its pre bellum quotations. Whereas, before the hostilities began, the common wholesale price of resorcin crystals was $ .80 @ $ .85 a pound it is now about ten times that amount. In Curve 1 is shown a record of the range of market prices of this material during the last four years, and is perhaps the most remarkable effect experienced by the market price of any of the materials previously manufactured almost exclusively in Germany.

About the first American manufacturer's advertisement for the production of resorcin


CURVE #1
35
30
25
20
15
10
5
0
PRICE - DOLLARS PER LB.
1914
1915
1916
1917
1918
YEAR
WHOLESALE PRICES OF RESORCIN
(OIL, PAINT AND DRUG REPORTER)
CABLE DREST 1918

appeared in the Oil, Paint and Drug Reporter about September 23 1916 , when the market price had risen to about $25.00 a pound. The market price continued to rise and reached its maximum at $35.00 a pound during the latter part of the same year. Beyond that time competition developed in this country in the manufacture of this material, causing a continual decline in the market price since then. It is interesting to compare the market price curve of resorcin with that of phenol, which is made by similar, but considerably easier, synthetic operations. The phenol price is found to start up almost immediately after the war was declared and rose so rapidly that on June 5, 1915 it actually exceeded the resorcin price, being on that date $1.50 a pound whereas the latter was quoted at $1.25 @ $1.30 a pound. This and the fact that the phenol price rose more suddenly than the resorcin price may be explained by the fact that the warfare created an excessive demand for phenol to be used in making explosives,

whereas resorcin was not used for any such purpose.

In studying this problem the authors attacked the problem in two ways. The first was an attempt to produce this compound by means of an original and yet untried method, which seemed to be theoretically possible. The other method of dealing with this problem was to study the present commercial methods of production with a view to finding the most favorable conditions of operation.

The authors wish to express their deep appreciation of the useful help in this work which they received from their friends, especially Professor Mc Cormack whose practical suggestions were of great value.

An Attempt to Produce Resorcin from m-Phenylenediamine by Means of the Bisulphite Conversion.

One of the reasons for selecting the subject of this thesis with which to work was to test the feasibility of producing resorcin by a theoretically possible and new method. This method was founded upon a series of reactions to which very meagre attention has been paid in the English chemical literature and is, perhaps, a developement of the last decade in the science of chemistry.

The only reference which was known to the authors prior to the initial investigations upon these reactions was the following brief mention made in the book of André Wahl on the "Manufacture of Organic Dyestuffs" as translated from the French by F.W. Attack and published in 1914:

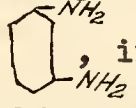
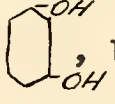
"Conversion of an amine into phenol or naphthol can be effected by treatment with an

excess of a solution of sodium bisulphite (sp. gr. - 1.32 to 1.38) and subsequently saponifying with aqueous alkali.

(1) $RNH_2 + NaHSO_3 = ROSO_2Na + NH_3$

(2) $ROSO_2Na + NaOH = RONa + Na_2SO_3 + H_2O$."

Proposed Proceedure

The method, then, which we proposed was to convert m-Phenylenediamine,  , into resorcin,  , by means of this general reaction. The details of the method which we proposed to investigate were as follows:

An aqueous solution of m-phenylenediamine and sodium bisulphite was to be made containing sufficient $NaHSO_3$ to give a solution of sp. gr. - 1.32 and with an excess of at least 50% of the theoretically required amount of $NaHSO_3$ for the quantity of the diamine used to allow the above reactions to proceed so as to replace both NH_2 groups by hydroxyl groups. This solution was to be made neutral to litmus paper by adding the required amount of H_2SO_4

and was then to be heated at 100°C a sufficient length of time to liberate the equivalent weights of NH_3 as given by reaction (1) with the simultaneous formation of $C_6H_4(OSO_2Na)_2$.

The solution was then to be heated with an excess of lime to drive off the above formed ammonia, giving also the di-Calcium salt, $C_6H_4(Oca)_2$, in which ca represents a one-half atomic weight of Calcium. The percipitated $CaSO_3$ and $CaSO_4$ was next to be filtered off, and the alkaline solution containing the $C_6H_4(Oca)_2$ acidified forming in solution the resorcin which could then be extracted by means of a suitable low boiling solvent such as ether.

We hoped to prove that this process if successful would be more desirable than the present process, because of the advantage which lay in the fact that in the former all reactions would be carried out at temperatures of 100°C or lower thus decreasing the tendency of forming tarry bodies together with the

resorcin as obtained in the present commercial method due largely to the high temperatures of fusion, ie. almost 300°C.

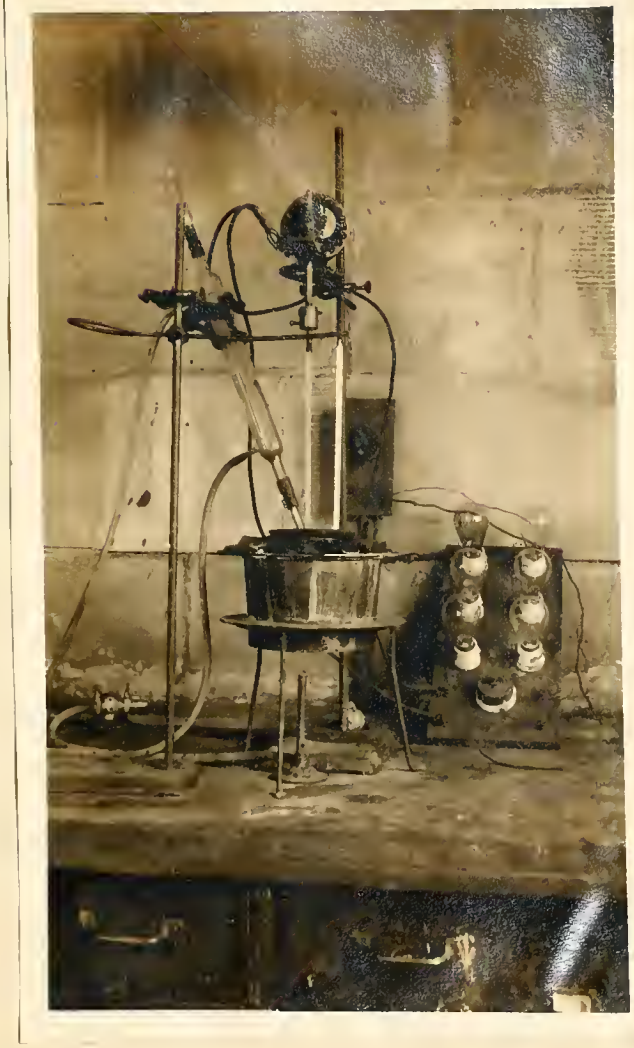
Experimental Work

With these ideas in view we obtained some m-phenylenediamine and tested its purity by the method given on p. 277 of the 1905 edition of Cain and Thorpe's "The Synthetic Dyestuffs and Intermediate Products from which they are Derived". Its purity was found by this analysis to be about 99%. The following solution was then prepared in an 800 c.c. beaker:

m-phenylenediamine (based on the pure body)	19.459 grams
sodium bisulphite	181.6 grams
water - sufficient to make 590 c.c. of solution of sp. gr. -	1.31(hot)

The apparatus which was used in the subsequent operations is shown assembled in Plate I, with an electrically driven agitator whose speed could be varied as desired by adjusting the

Plate I

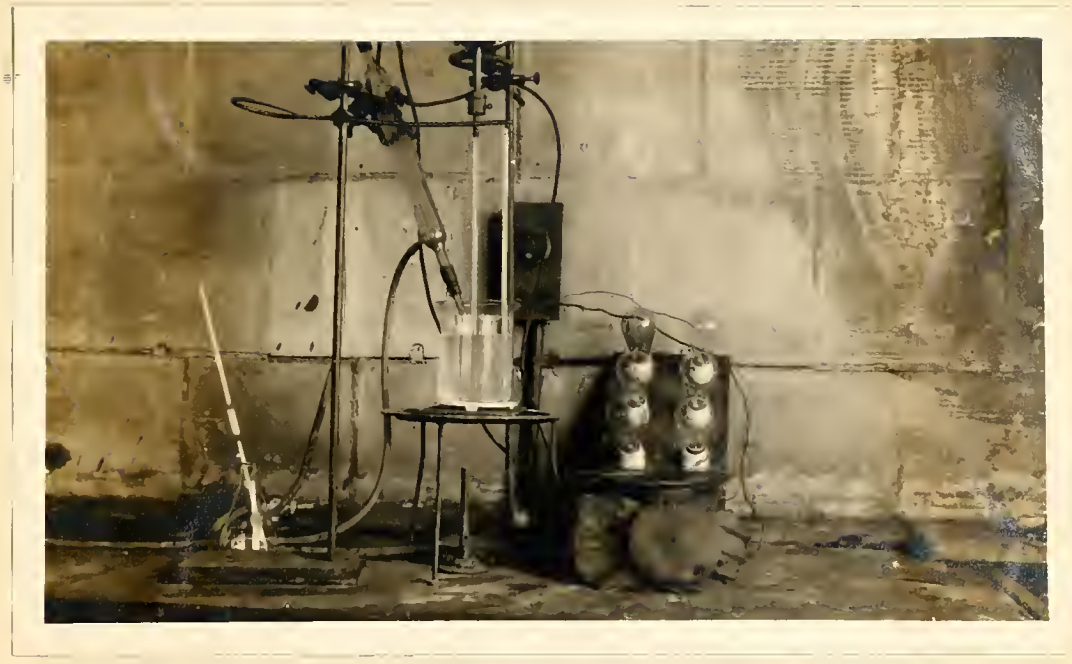


Apparatus for bisulphite reactions

resistance of the lamp rack connected in series between motor and 110 volt D.C. house line. The beaker containing the above solution was covered with a sheet of para rubber having a hole in its center for glass agitator shaft, and also holes near the sides for the insertion of reflux condenser, and a thermometer. The function of this cover and reflux condenser was to prevent excessive evaporation at the elevated temperatures of operation as is desired in minimizing the volume change in order to know most accurately the volume of solution at the time of making control runs.

In order to maintain as uniform conditions of temperature as possible, the beaker was supported in a slowly boiling brine bath at a closely regulated temperature of 99 to 101°C. Plate II gives a better view of the beaker in position with rubber cover and water bath removed. On the left is shown a 5 c.c. pipette and 250 c.c. ehrlenmeyer flask with which samples of the solution were taken during the course of the cooking

Plate II

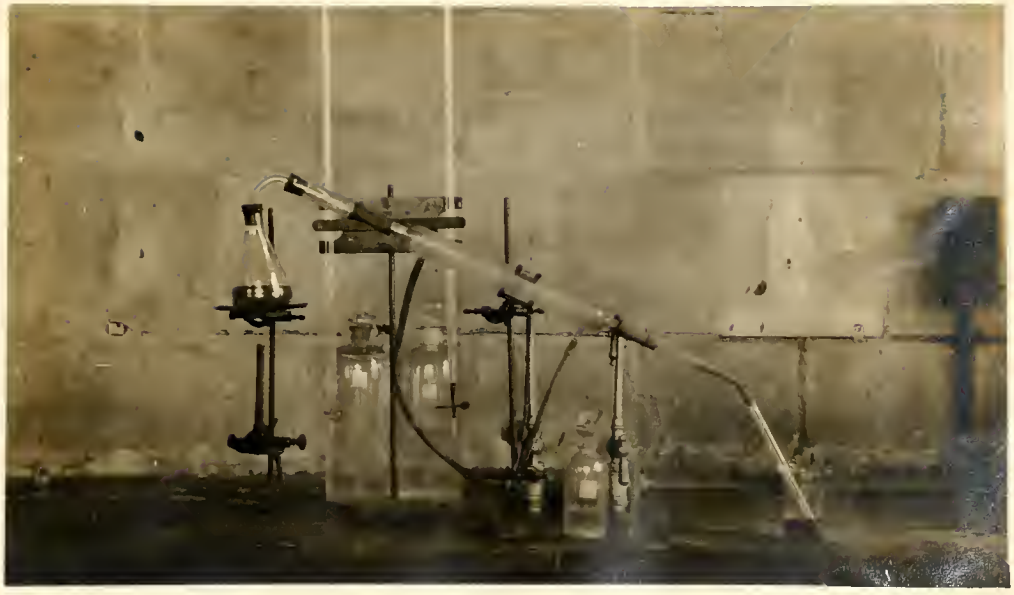


Bisulphite Apparatus (Water bath removed)

operations for determining the progress of the reaction.

An interesting feature of this conversion operation lies in the fact that a very accurate determination can be made of the degree of completion of the reaction by a simple ammonia determination since we see from reaction (1) that for every sulphite ester group attached to the nucleus a corresponding molecule of ammonia is subsequently liberated when an aliquot portion of the total solution is introduced into a distilling apparatus as shown in Plate III and made strongly alkaline with NaOH. The ammonia which is liberated is quantitatively determined by being distilled into a beaker containing a known quantity of acid, followed by titration with a standard solution of alkali. In making these control runs five c.c. of the solution were drawn out of the beaker while the agitator was still in motion and run into a 250 c.C. ehrlenmeyer flask. About 80 c.c. of water was added and then ten c.c. of concen-

Plate III



Apparatus for making control runs.

trated NaOH solution. For standard acid solution in the receiving beaker a 1.000 x N/10 solution of H_2SO_4 was employed. The back titration was made with 1.000 x N/10 NaOH. The resulting data which was obtained on our first run is shown in Table 1.

The results are graphically represented in Curve 2 which shows a progressive conversion of m-phenylenediamine into m-phenyleneamino-sulphite ester. The reaction then seems to stop with the displacement of one of the NH_2 groups of the diamine by the corresponding monosulphite ester group. From this it would seem reasonable to suppose that the displacement of the other ammino group is either impossible or requires a more vigorous treatment with bisulphite than given.

Considering a possibly more favorable condition for displacing the second NH_2 group by substituting the hydroxyl group for the sulphite ester group through saponification with alkali, this operation was performed using

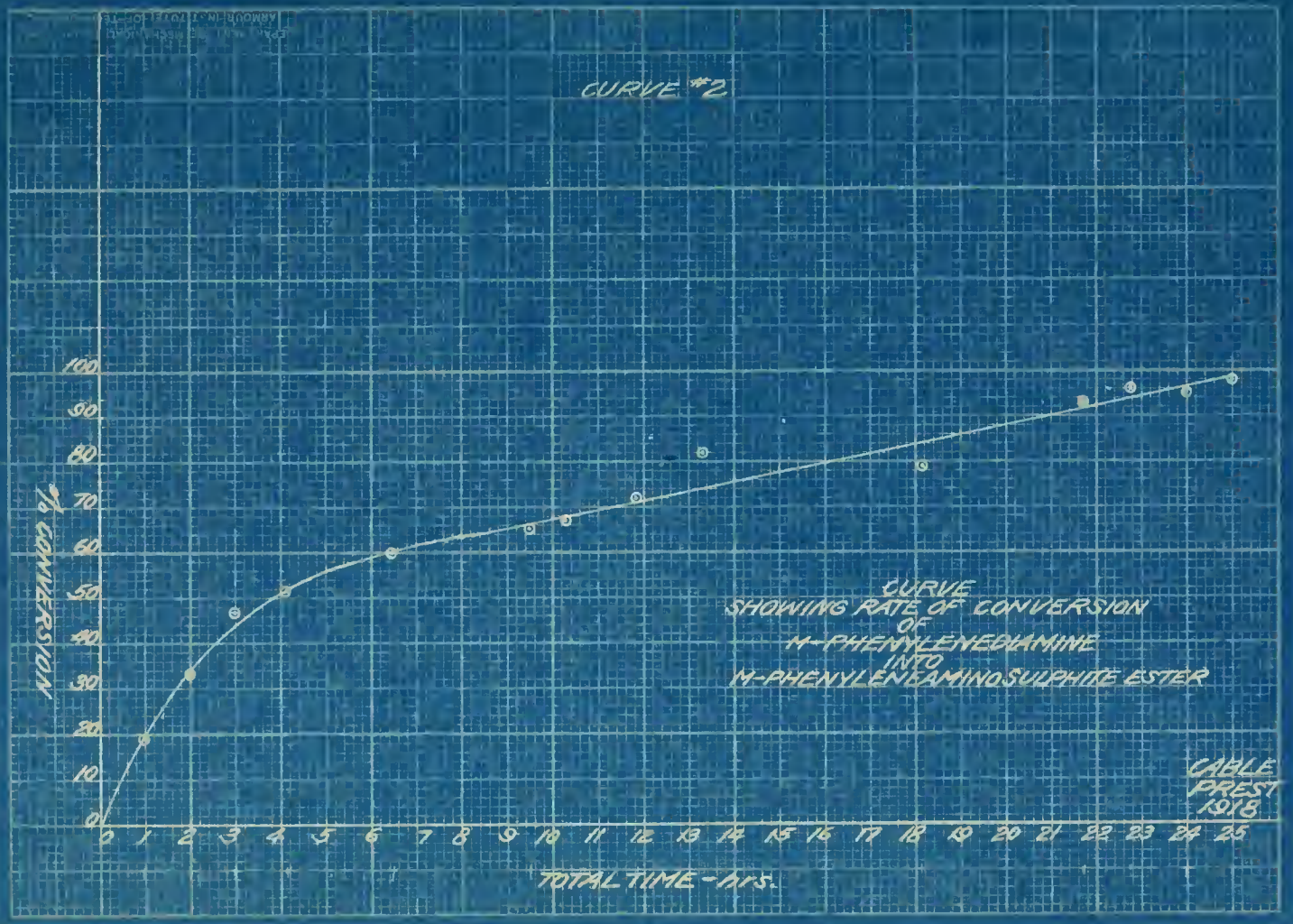
TABLE 1

DATA ON BISULPHITE CONVERSION OF M-PHENYLENEDIAMINE INTO M-PHENYLENEAMINOSULPHITE ESTER

All samples measured out in 5 c.c. pipette. Weight of m-phenylenediamine which if completely converted into m-phenyleneaminosulphite ester would liberate sufficient NH_3 to neutralize 50 c.c. of 1.000 × N/10 H_2SO_4 = $\frac{108.2 \times 50}{1000 \times 10}$ = 0.541 grams.

Time recorded sr-started sp-stopped	Total time		Wt. of m phenylene-diamine in beaker or its equivalent, gms.	Volume of solution, c.c.	Wt. of m phenylene-diamine in Sample, gms.	No. c.c. of N/10 H_2SO_4 used	No. c.c. of N/10 NaOH used	Net c.c. H_2SO_4 required	% conversion of m-phenylenediamine into above ester
	hours	min.							
sr 12:20 4-11-18			19.459	590					
1:20 P.M.	1	0	19.459	580	.168	10.00	7.03	2.97	19.2
2:20 P.M.	2	0	19.291	570	.169	10.00	4.80	5.20	33.2
3:20 P.M.	3	0	19.122	560	.171	10.00	2.64	7.36	46.6
4:30 P.M.	4	10	18.951	548	.173	10.30	2.18	8.12	51.0
sp 4:50 P.M.	4	30	18.778	543					
sr 9:30 4-15-18	4	30	18.778	543					
11:30 A.M.	6	30	18.778	511	.183	12.09	2.00	10.09	59.6
2:30 P.M.	9	30	18.595	463	.201	12.05	0.00	12.05	65.0
sp 4:50 P.M.	11	50	18.394	428	.214	14.40	0.11	14.29	72.2
sr 10:30 4-16-18	11	50	18.180	428					
12:00 M	13	20	18.180	393	.231	17.57	0.17	17.40	81.6
sp 4:50 P.M.	18	10	17.949	280	.320	24.30	0.91	23.39	79.0
sr 10 AM 4-17-18	18	10	17.629	462					
1:30 P.M.	21	40	17.629	420	.210	18.30	0.25	18.05	93.4
2:35 P.M.	22	45	17.419	408	.214	19.10	0.20	18.90	95.8
3:50 P.M.	24	0	17.205	391	.220	19.65	0.30	19.35	95.4
4:50 P.M.	25	0	16.985	380	.223	20.17	0.00	20.17	98.0

D.E.C.


CURVE #2
% CONVERSION
100
90
80
70
60
50
40
30
20
10
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25
TOTAL TIME - HRS.
CURVE
SHOWING RATE OF CONVERSION
OF
M-PHENYLENEDIAMINE
INTO
M-PHENYLENEAMINOSULPHITE ESTER
CABLE
PREST
KOI8

70 grams of NaOH and saponifying with uncovered beaker to allow the escape of the liberated ammonia. This saponification was carried out for about seven hours. On the following morning the solution was neutralized (neutral to litmus) with H_2SO_4 whereby the sodium sulphite present in the alkaline solution was recovered into sodium bisulphite.

The bisulphite reaction was allowed to ensue as in the previous case, control runs being made as usual. The data obtained from this second conversion shown in Table 2 indicates but a small degree of conversion into the disulphite ester and practically no appreciable progression in the tendency to form such ester. The obvious conclusion to be drawn from these experiments is that the proposed method is not feasible under the conditions of reaction attempted, because of the impossibility of replacing more than one of the ammino groups of m-phenylenediamine by an hydroxyl group.

TABLE "2

DATA ON BISULPHITE CONVERSION OF M-AMINOPHENOL INTO M-PHENYLENEDISULPHITE ESTER

All samples measured out in 5 c.c. pipette. Weight of m-aminophenol which if completely converted into m-phenylenedisulphite ester would liberate sufficient NH_3 to neutralize 50 c.c. of 1.000 x N/10 H_2SO_4 = $\frac{109.1 \times 50}{1000 \times 10}$ = 0.5455 grams.

Time recorded sr - started sp - stopped	Total time		Wt. of m. aminophenol in beaker or its equivalent, grams.	Volume of solution, c.c.	Wt. of m. aminophenol in sample, grams.	No. c.c. of N/10 H_2SO_4 used	No. c.c. of N/10 NaOH used	Net c.c H_2SO_4 required	% conversion of m-aminophenol into above ester
	hours	min.							
Sr 10 A.M. 4-22-18			16.890	548					
10:20 A.M.		20	16.890	544	.155	3.50	2.74	0.76	5.38
2:35 P.M.	4	35	16.735	489	.171	3.05	2.29	0.76	4.84
Sp 4:50 P.M.	6	50	16.564	465	.178	3.07	2.12	0.95	5.80
Sr 11 A.M. 4-23-18			16.386	502					
3:00 P.M.	10	50	16.386	450	.182	3.00	1.96	1.04	6.22

D.E.C.

The authors discovered after having performed the above work a very complete discussion in Dr. Hans Th. Bucherer's "Lehrbuch der Farbenchemie" (1914) on the bisulphite conversion reactions with which we were dealing. According to Bucherer, " It is of theoretical interest to one regarding the application of the sulphite reaction, but many very difficultly explained exceptions are obtained. Whereas, indeed, in numerous cases the reaction is unusually rapid and proceeds smoothly, for instance with the 1,4 naphthol sulpho acid, the reaction is denied - one can say entirely if one deals with certain isomers of naphtholsulpho acid. The reaction is denied which principally applies to the derivation of α - naphthol, to the 1,2-naphtholsulpho acid; even also to the 1,2,5-, 1,2,6-, 1,2,7-, 1,2,8-, as with 1,3,5-, 1,3,6-, 1,3,7-, 1,3,8-naphtholsulpho acids. All these derivatives of 1,2- and 1,3- naphtholsulpho acids do not react with bisulphite, and no doubt do not inasmuch as they are not capable

of forming the sulphite ester."

Another English reference was also found which throws some light upon this subject. Sidgwick in his "Organic Chemistry of Nitrogen" gives a short discussion of the bisulphite reaction, concluding by saying "Fatty amines and alcohols do not give these reactions at all; and even the benzene derivatives do so much less readily than those of naphthalene." In view of the exceptions mentioned by Bucherer with reference to the naphthalene compounds and also Sidgwick's statement that the benzene derivatives react much less readily than the naphthalene derivatives the results which we obtained are reasonable to expect.

Part II

Present Commercial Method of Producing Resorcin.

The new method, which we originally proposed, having been found to be unfeasable our further efforts were exclusively devoted to a superficial study of the present commercial process of manufacturing resorcin. As neither of the authors have had any actual experience in a commercial plant in making resorcin, the methods of the following investigations must necessarily be guided by the information gleaned from the chemical literature upon this subject.

Theoretical Considerations

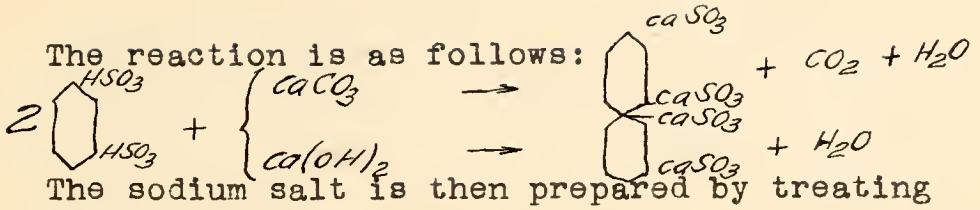
When benzol is heated with strong sulphuric acid, either the mono or disulphonic acids are produced, depending upon the conditions under which the sulphonation is carried out. If the acid is 64° Bé acid and the temperature is moderate, the mono sulphonic acid is produced. The disulphonic acid may then be produced by

further heating at a temperature near 250°C. These two operations may be combined into one by heating the benzene with fuming sulphuric acid, first at a low temperature for a short time and then for a greater length of time at 275°C.

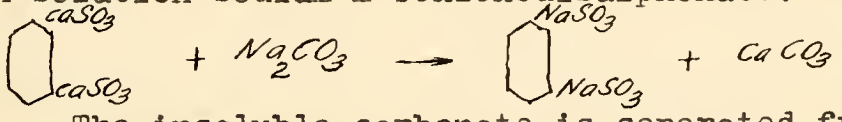
The reaction is as follows:

In the disulphonate formation, the substitution follows the general rule, and the main product is the meta compound. The disulphonic acid may be seperated from the excess sulphuric acid by adding soluble bases of the metals calcium, barium or lead. The seperation is due to the formation of soluble salts of H_2SO_4. The general practice is to use $CaCO_3$ percipitate and slacked lime, the former being obtained as a by-product in a succeeding operation. On filtering, the calcium sulphate remains on the filter, while the calcium salt of the disulphonic acid remains in the filtrate.

The reaction is as follows:



The sodium salt is then prepared by treating the calcium m-benzenedisulphonate with Na_2CO_3. The calcium is precipitated out as $CaCO_3$ leaving in solution sodium m-benzenedisulphonate.



The insoluble carbonate is seperated from the soluble sodium m-benzenedisulphonate by filtration and is used as indicated above to help neutralize the sulphonation mixture. The filtrate containing the sodium salt of the disulphonic acid is then evaporated to the seperation of the sodium compound which is then thoroughly dried.

The dried sodium m-benzenedisulphonate is fused with an excess of NaOH, the sulpho-radicals being removed and the sodium salt of resorcin formed. This reaction proceeds as follows:

It is a remarkable fact that the sodium p-benzenedisulphonate on similar fusions gives the same product, sodium m-diphenate, as the meta compound.

The resorcin may then be obtained by acidifying an aqueous solution of the fused mass. The excess alkali used in the fusion is neutralized and the Na atoms of the diphenate replaced by H atoms according to the following reaction:

$$C_6H_4(ONa)_2 + 2\ HCl \rightarrow C_6H_4(OH)_2 + 2\ NaCl.$$

The resorcin is then extracted by means of organic solvents and purified by sublimation or vacuum distillation.

Experimental Work

In the experiments that were carried out by us the resorcin was made from commercial sodium m-benzenedisulphonate which was supplied to us through the courtesy of The Barrett Co. and was stated by them to be an "extremely highly refined material, possibly containing as impurities small amounts of mono Sulphonate,

Sodium Sulphate, Sodium Carbonate and Calcium Sulphate".

In the discussion of the experimental work that follows, no details of the process up to the formation of the sodium disulphonate will be given. The discussion of the work will be divided into the following parts:

1. Fusion of the sodium m-benzene disulphonate.
2. Acidification of the fusion to form resorcin.
3. Extraction of the resorcin.
4. Purification of the resorcin.

These experiments were undertaken with the idea of determining the most economical means of production.

1. Fusion of the sodium m-benzenedisulphonate:

The conversion of the disulphonate body into the diphenate body is accomplished by fusion with NaOH. There are two common ways of making this

fusion: first, in an open kettle; second, in an autoclave. The first is the one described to the greatest extent in the literature. The second method of making a fusion in an autoclave is given in an article by A.H. Ney and D.J. Van Marle on "The Processes of the Organic Chemical Industry Used in the Manufacture of Intermediate Products", published in the Metallurgical and Chemical Engineering Magazine, February 15, 1917.

"Caustic fusion with water is carried out in autoclaves under pressure, which allows the amount of caustic soda to be cut down materially and prevents oxidation. . . . . In the case of di- and trisulphonic acids, however, a much larger excess of caustic soda has to be used (than in the case of mono-sulphonic acids) and here generally the use of autoclaves will be preferred. These products at the same time are the more expensive ones, and mostly not prepared in such large amounts. In these higher sulphonic acids the sulphonic acid groups are not all at

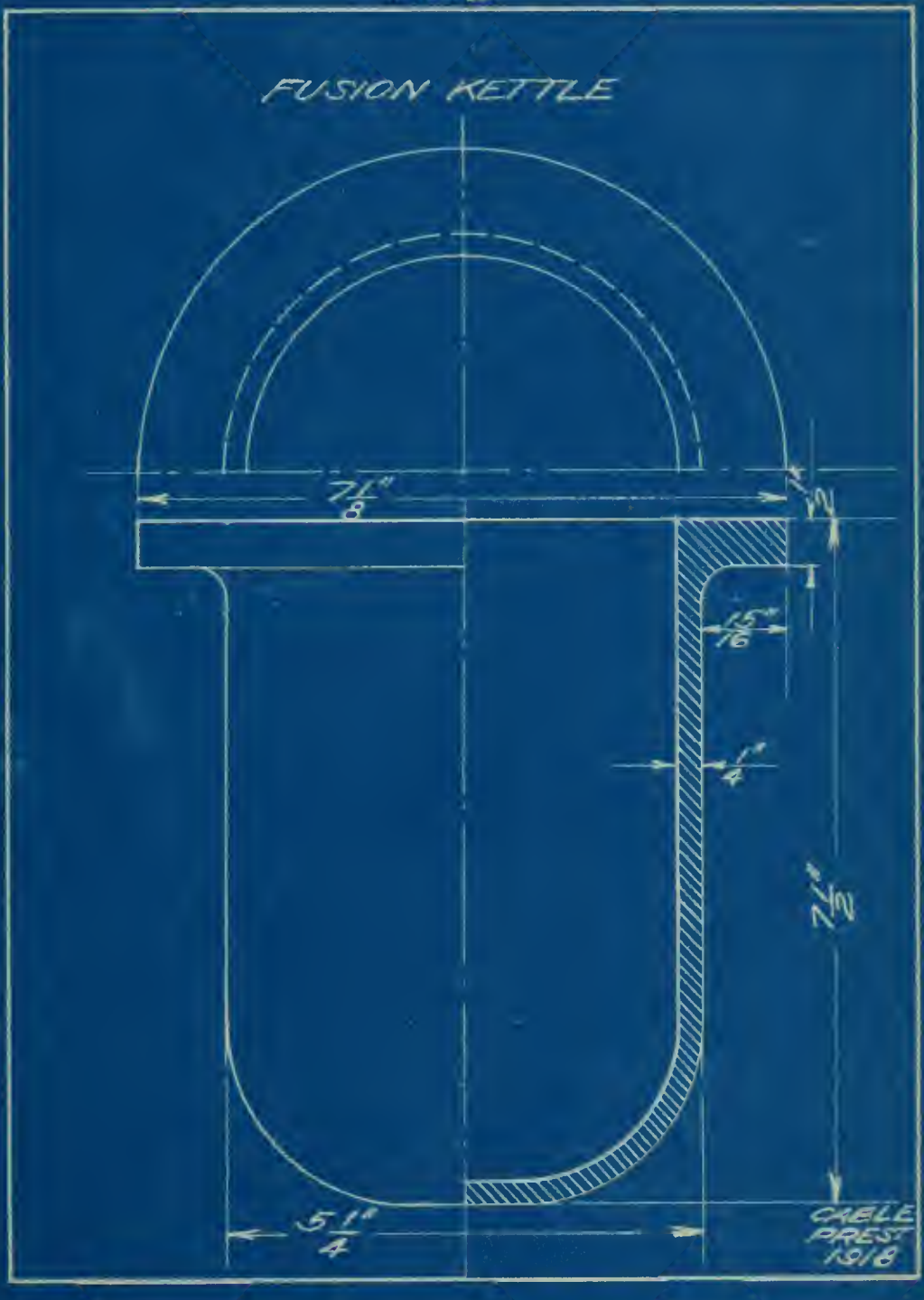
once replaced, benzene m-disulphonic acid, for instance, first being converted into phenol m-sulphonic acid, then into m-dioxybenzol or resorcin. . . . .

"Caustic fusions are carried out either in open cast iron kettles, in which the caustic soda is fused and the sodium sulphonate gradually added or in autoclaves under pressure. . . . . Both autoclaves and fusion kettles are provided with an agitator and are placed in a furnace, which is heated by oil or gas, as the temperature to which the mixture is heated is often above 300°C."

Since no autoclave with agitator was available for use in this laboratory, the fusions in this work were entirely made in the open cast iron type of fusion kettle shown in Fig.2.

The fusion mixture used in these experiments was 2 1/2 parts of caustic soda to 1 part of sodium m-benzenedisulphonate which is that most commonly recommended in the literature on this process.

FIG. 2



According to the calculations based on the following equation 0.6 part of alkali is required to 1 part of sodium m-benzenedisulphonate.

$$C_6H_4(SO_3Na)_2 + 4NaOH \rightarrow C_6H_4(ONa)_2 + 2Na_2SO_3.$$

$$\frac{4\ NaOH}{C_6H_4(SO_3Na)_2} = \frac{X}{1}$$

$$X = \frac{1 \times 160}{282} = 0.57$$

2.5 lbs. NaOH used for 1 lb. of $C_6H_4(SO_3Na)_2$

2.5 - 0.57 = 1.93 lbs. excess used. These calculations show that four times the theoretical amount of caustic soda was used.

The temperature to be used in the fusion is usually recommended as 270 - 280°C. In these experiments, the temperature ranged from 280 to 310°C.

The length of time required for the fusion is usually given as 7 - 10 hrs.. In these experiments the length of time for the fusion was from 1 1/2 to 4 1/2 hours.

The apparatus was assembled as shown in Plate IV. The kettle was supported over a Rose burner by means of a stand. 2 1/2 pounds of

Plate IV

Apparatus used in making fusions

NaOH were placed in the kettle and melted. The fire end of a calibrated Hoskins base metal pyrometer was then inserted into the fused caustic soda, and the temperature was regulated to that at which the fusion was to be carried out. One pound of the pulverized sodium m-benzene-disulphonate was gradually added to the caustic soda, each portion being allowed to dissolve before any more was added. The fusion was then continued for the required length of time, care being taken to maintain as nearly a uniform temperature as possible. Four fusions were thus made.

The first fusion was made at a temperature of 305 -310°C for 1 1/2 hours. The melt was poured into a small quantity of water. All of the fusion except a small amount dissolved in the water.

The second fusion was made at a temperature of 305°C for one hour and at 315 - 320°C for one-half an hour. The melt was poured into iron pans and allowed to solidify.

The third fusion was carried out at a temperature of 310°C for 2 1/4 hours. This melt was poured into iron pans as in the previous fusion.

The fourth fusion was made at a temperature of 280°C for 4 1/2 hours and was then ladled into water.

In fusions 2 and 3 the solidified mass was colored brown and was very hard, causing considerable difficulty in bringing it into solution.

2. Acidification of the fusion to form resorcin:

The liberation of the resorcin is accomplished by adding acid to the mixture of NaOH and sodium diphenate. This operation may be carried out either in a water solution of the two materials or by directly adding the acid to the solidified mass. Mineral acids like HCl or H_2SO_4 may be used, or if the diphenate is in solution CO_2 gas may be used. Concentrated HCl was used in these experiments; and the acid was added to the solidified melts of 2 and 3,

and to the fusion solution in 1 and 4.

According to calculations based on the following equations 2035 c.c. of the concentrated HCl was required.

$$C_6H_4(ONa)_2 + 2\ HCl \rightarrow C_6H_4(OH)_2 + 2\ NaCl.$$

$$\frac{2\ HCl}{C_6H_4(ONa)_2} = \frac{X'}{0.595}$$

$$X' = \frac{73 \times 0.595}{188} = 0.23 \text{ lbs. HCl}$$

$$NaOH + HCl \rightarrow NaCl + H_2O$$

$$\frac{36.5}{40.0} = \frac{X''}{1.93}$$

$$X'' = \frac{1.93 \times 36.5}{40} = 1.74 \text{ lbs. HCl}$$

$1.74 + 0.23 = 1.97$ lbs. HCl, total reqd.

$1.97 \times 454 = 895$ grams required.

HCl used:- sp. gr. - 1.19, % HCl - 37 (label)

$0.37 \times 1.19 = 0.44$ gms. HCl per c.c.

$$\frac{895}{0.44} = 2035 \text{ c.c. required.}$$

The acid was added until the solution showed acid reaction as indicated by Congo Red test paper. The amount of acid used in our experiments was generally about 2200 c.c.

The properties of the acidified mixture

varied with the different fusions. The color of the solutions varied from a dark red in the first three fusions to a light yellow in the fourth fusion. The solutions had a strong odor of SO_2 due to the reaction between some of the sodium sulphite formed in the fusion with the slight excess of acid. A heavy white precipitate settled out of the acidified solution and was removed by filtration.

3. Extraction of the resorcin:

The separation of the resorcin from the acid liquor is accomplished by extraction with organic solvents. The two most commonly used solvents for this purpose are ether and amyl alcohol. The high price of these solvents caused us to investigate other low boiling solvents to see if any of them might be as satisfactory.

The solvents which we investigated were toluene, chloroform, terpentine, amyl alcohol, benzol, ether and benzyl chloride. The results obtained showed that ether and amyl alcohol are

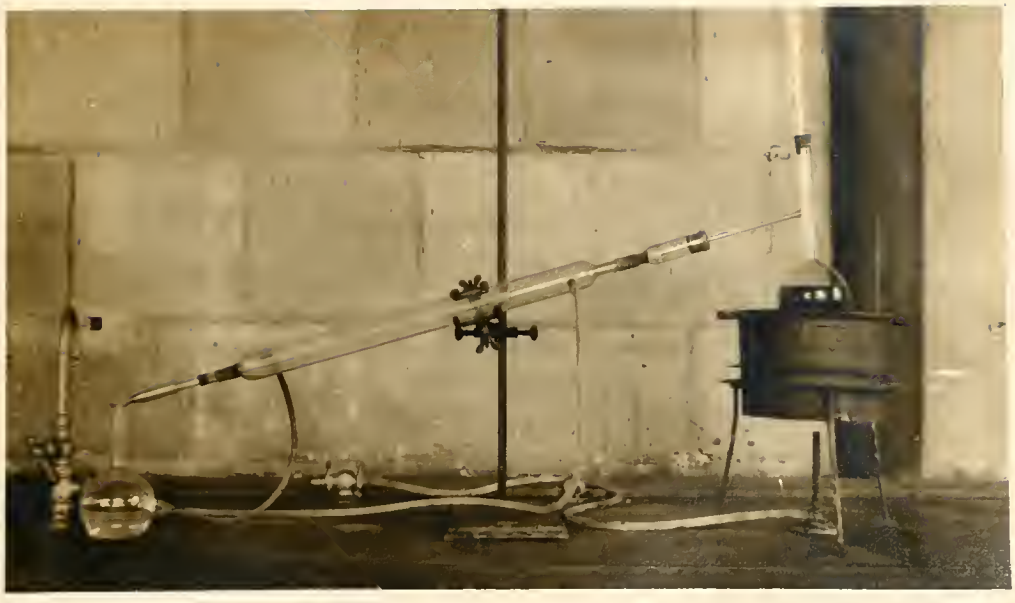
the only solvents in the list given in which resorcin is very soluble. The amount of resorcin extracted by the other solvents was very small. Hence the choice between amyl alcohol and ether seemed the only question to settle. Because of the considerably greater cost of amyl alcohol as compared to ether and in view of the extreme solubility of resorcin in the latter we decided to use it exclusively in our experiments.

400 c.c. of the aqueous solution of resorcin after acidification was twice extracted with 200 c.c. of ether. This operation was repeated until all of the solution had been extracted. The total ether extract was then distilled over a water bath to remove the ether leaving the resorcin as a residue in the distilling flask. The arrangement for this distillation is shown in Plate V.

4. Purification of the resorcin:

There are two common methods available for the purification of resorcin; sublimation and vacuum distil-

Plate V



Ether distillation apparatus

lation. The method used in this investigation was sublimation.

The residue from the ether extract was placed in a glass retort and heated on a sand bath. The crystals were caught in the neck of the retort. In order to force the resorcin vapors into the neck of the retort, a slow stream of dried air was blown thru' the system. At intervals, as the neck became filled with the rhombic plated crystals of resorcin the retort was removed from the sand bath and the crystals collected. This operation was repeated until all the original resorcin had been sublimed, leaving a tarry residue in the bulb of the retort.

The resorcin from the ether extract of the first three fusions was colored a dark red, while the residue from the fourth fusion was of a considerably lighter color. In the sublimation of the first three residues after the temperature had been raised to a point where vapors of resorcin should have been

evolved but a very small quantity appeared. After several trials it was appearent that only a small amount of resorcin was present and that the greater portion of the extract was resinous matter These residues were consequently abandoned.

The residue from the fourth fusion was the only one which furnished any good yield of resorcin, and this was completely sublimed, giving 40 grams or 0.08 lb. of resorcin. The theoretical yield based on the following equation is 0.35 lb. Thus the efficiency of our fourth yield was 22.8%.

$$\frac{C_6H_4(OH)_2}{C_6H_4(SO_3Na)_2} = \frac{X}{1}$$

$$X = \frac{1 \times 110}{316} = 0.35 \text{ lb.}$$

Mühlhausen and Wagner state that the yield of resorcin based on 125 kilograms of sodium m-benzenedisulphonate is 20 to 23 kilograms. This is equivalent to 55 - 63 grams or 0.12 - 0.14 lb. of resorcin per pound of sodium

benzene disulphonate or to an efficiency of 34.3 - 40%.

Because of the limitation of time we considered further experimentation upon the production of resorcin by this method to be out of the question, since all of the operations involved from making the fusion to the final purification of the extracted product required exceptionally long periods of time. Undoubtedly our yield in the fourth fusion would have been considerably improved had we extended the fusion period from 4 1/2 hours to twice that time.

The authors attempted to make a vacuum distillation of some pure resorcin, but found that such an operation was almost impossible in using ordinary glass distillation apparatus, because of the unavoidable tendency of the resorcin to solidify in the glass delivery tubing where covered with rubber stoppers, the high melting point of the resorcin (118°C) being the reason for this. In the above mentioned

article by Ney and Van Marle the method used commercially for purifying the resorcin is stated to be by vacuum distillation. This method seems most satisfactory to the authors because of the more complete isolation of the pure compound by this method and also because of the tendency for oxidation and formation of tarry residues when performing a sublimation as conducted in our experiments.